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(54) Title: PICKLING PROCESS AND PRODUCT

(57) Abstract

Crisp textured pickled foodstuffs and a method in which foodstuffs are pickled in a nonfermentative process in less than about 72 hours by infusing the foodstuff with more than about 1000 ppm calcium. In one embodiment the foodstuff is infused with the calcium in a very short time period by subjecting the foodstuff, while immersed in a high calcium concentration brine, to a reduced pressure environment and ultra-sonic sound waves. In another embodiment, the brine immersed foodstuff is frozen in the brine.

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PICKLING PROCESS AND PRODUCT

BACKGROUND OF INVENTION

Most current pickling fermentation/salt brining processes have three major negative factors :

1. A very high brine sodium chloride content (e.g., for pickling cucumbers the brine is 5-8%, by weight, sodium chloride during fermentation, and 8-16% sodium chloride during storage). Such high brine sodium chloride contents may necessitate a "desalting" prior to shipping to reduce the sodium chloride level to 3-4%. Moreover, the disposal of the brine may be environmentally harmful. At a final sodium chloride content of about 3.5%, an average pickled cucumber piece weighing 3 oz (85 g) contains 2.9 g sodium chloride.

2. An uncontrolled process. Uncertainties inherent in the fermentation result in inconsistent product quality and frequently an unmarketable product.

These uncertainties are due to:

i) Natural (or "wild") fermentation. Fermentation can begin before controlled fermentation conditions are established;

ii) Enzymatic softening (pectinolytic, etc.). During the initial stages of brining/fermentation, the green stock's endogenous enzymes can break-down the green stock's structural

iii) Structural damage and bloating. Microorganisms, initially present in the green stock -- i.e., gram positive and negative bacteria, yeasts, oxidative yeasts and molds -- release gases which may cause structural tissue damage and bloating in fermentation processes. Furthermore, the green stock's respiration can also produce carbon dioxide and hydrogen.

3. A complicated and time consuming process. For example, traditional fermentation of cucumbers may involve:

- i) Cleaning the cucumbers with water and chlorine sanitation prior to brining;
- ii) Acidifing the green stock;
- iii) Purging the green stock with Nitrogen;
- iv) Salting - concentration between 5-8% sodium chloride is typically added to the pickling solution to adjust the pH of the pickling solution;
- v) Buffering;
- vi) Addition of the "fermenting" culture;
- vii) Fermentation - may require from about 7 to 90 days to complete;
- viii) Further salting a 8-16% brine solution is commonly used to preserve the "pickle" during storage;
- ix) "Desalting" prior to being shipped to the consumer, the "pickle" must be "desalted" to reduce the brine product sodium chloride content to 3 to 4%;
- x) Packaging the "pickle" in jars or cans; and
- xi) Pasteurization.

In traditional fermentation pickling process for cucumbers, *Lactobacillus plantarum* pass through the skin of the green stock and enter into the inner tissues of the green stock. The green

stock is immersed in a 5-18% sodium chloride brine which diffuses into the green stock during fermentation. During the fermentation process, *L. plantarum*, which can tolerate high salt levels, metabolizes carbohydrates both within and without the green stock. This *L. plantarum* metabolism produces lactic acid (up to 0.6% of the brine) and acetic acid (up to 0.2% of the brine), which metabolic products diffuse out of the green stock. Also during fermentation, other materials such as soluble tissue components including sugars, diffuse out of the green stock.

In addition to producing lactic and acetic acids, *L. plantarum* metabolism produces carbon dioxide. As this carbon dioxide is in addition to the carbon dioxide, nitrogen and oxygen initially present in the green stock and brine, the brine will contain 6% or more carbon dioxide. As the carbon dioxide can diffuse into and out of the green stock much faster than nitrogen and oxygen can diffuse out of the green stock -- carbon dioxide is much more water soluble than either nitrogen or oxygen -- the entrapped nitrogen and oxygen rupture the soft middle sections of the green stock and form voids.

In traditional pickling process, green stock is softened both before and after fermentation. Prior to fermentation and during the slow initial diffusion of sodium chloride into the green stock, the green stock's endogenous polyglacturonase hydrolyzes pectins within the green stock, breaking down the green stock's structural components. After fermentation, when the "pickle" is in a 3-4% salt brine, the green stock's endogenous polyglacturonase activity can resume and further break-down structural components of the green stock.

It is an object of the present invention to provide a non-

stantially instantaneously and which process reduces the negative aspects found in some current pickling processes.

It is another object of the present invention to provide a method for manufacturing a pickle having a low level of sodium chloride compared to the pickles currently on the market.

It is a further object of the present invention to provide a method for manufacturing pickles in a shorter time than was heretofore possible.

It is yet another object of the present invention to provide a method for manufacturing pickles in a manner that readily controls those operating parameters which can reduce the yield of the process.

It is a still further object of the present invention to provide a pickle having a very high calcium level.

DESCRIPTION OF THE INVENTION

The process of the present invention comprises dissolving water/acid soluble compounds and dispersing water/acid insoluble ingredients so as to form an aqueous pickling media which comprises at least about 1500 ppm Ca^{2+} . The to be pickled foodstuff or green stock is substantially immersed in said aqueous pickling media. The immersed green stock is then treated in a manner effective to rapidly infuse the green stock with an added Ca^{2+} concentration in excess of about 700 ppm Ca^{2+} . Preferred means of treating in a manner effective to rapidly infuse the green stock with added Ca^{2+} are either freezing the immersed green stock or placing the immersed green stock in a reduced pressure environment. In some embodiments of the present invention, the immersed green stock is also subjected to an ultra sonic treat-

ment. This process produces a product which comprises, inter alia, more than about 1000 ppm Ca^{2+} of which at least about 700 ppm Ca^{2+} is not endogenous to the green stock.

For illustrative purposes, the present disclosure generally sets forth practices and process variables and mechanisms for making "dill pickles" from cucumbers. However, it is believed that the method of the present invention can be used to pickle a wide variety of vegetables and meat/meat based products (herein "green stock") such as cucumbers, red and green peppers, green tomatoes, corn, cabbage, mushrooms, cauliflower, carrots, beans, beets, olives, horseradish, as well as calf/beef tongues, sausages, wieners and some small parts of pork. While the optimum conditions (including the brine composition) may, when the green stock is not cucumbers, differ from the conditions described herein, it is believed that the conditions described herein are operative for all green stock. Additionally, it is preferred that the green stock used is fresh, healthy vegetable and/or meat products.

The green stock treated in the process of the present invention may be whole, halved, quartered, cut into chunks, cut into slices or diced. However, when the green stock has a "skin" which skin substantially impedes the infusion of dissolved solids (including salts, acidulents and flavorings) and calcium ions into the green stock, it is preferred that the green stock is pricked in a manner effective to allow rapid dissolved solids and calcium infusion into the green stock. Thus, whole cucumbers may be pricked at least about 16 times in an approximately uniform distribution of pricks.

The process of the present invention is based on direct acidification/curing/preservation of green stock. The present process is believed to utilize the following functionalities:

1. Rapidly infusing acidulants, salt, and calcium salts (and optionally flavor and preservative) into the green stock; preferably, the infusion is substantially instantaneous.
2. Inhibiting microbial and fungal growth by the use of acidulants and by, concurrent with the infusion into the green stock, removing the free reducing sugars and carbon dioxide gas. The removal of these materials from the green stock may also inhibit traditional pickling/fermentation processes.
3. Strengthening the green stock's texture by calcium cross-linkages. The divalent calcium ions are believed to form a salt bridge with the carboxyl groups of the green stock's pectin.

The discovery that brine comprising about 760 ppm calcium produces a firm, chewy texture in green stock is set forth in U.S. Patent application Serial No. 765,177, which patent application is hereby incorporated by reference, led to a rapid non-fermentative process for pickling green stock. Calcium -- about 363 ppm of added calcium -- is believed to bind pectins in the green stock's tissues during that process. This calcium is in addition to the calcium that is naturally present in the fresh green stock.

The natural calcium level for each "species" of green stock varies with the growing region, growing time, and cultivar. For example, some fresh cucumbers have been found to have an endogenous calcium level of 166 ppm, while some other fresh cucumbers were calculated to have an endogenous calcium level of about 303 to 321 ppm.

In the process of the present invention, brines containing at least about 1500 ppm calcium, preferably at least about 2000 ppm calcium, and most preferably at least about 2500 ppm calcium are used to cure the green stock. These brines led to products containing preferably at least about 1000 ppm calcium, more preferably at least about 1500 ppm calcium, and most preferably at least about 2000 ppm calcium.

Calcium materials useful in the present invention comprise water/acid soluble calcium salts, such as calcium chloride, calcium nitrate, calcium sulfate, calcium oxide, and calcium acetate, lactate and gluconate.

Calcium ions binding of green stock pectinaecous substances according to the process of this present invention results in the following interrelated phenomena: The calcium maintains and strengthens the uniform inner tissue structure of the green stock. The resulting green stock's structural integrity slows down the rate of diffusion of reducing sugars from the green stock into the brine. During brining, calcium from the brine diffuses into the green stock and binds the green stock's pectin. The calcium binding of the green stocks' pectin precludes pectinolytic hydrolysis, even in low salt brines.

Fast, even firming of the green stock's tissues is effected by cross-linking the large pectin strands with calcium. This calcium level also retards fermentation in regular (8-12% by weight), low (1-2%) a no salt (0%) brines. (In a no salt brine, potassium chloride replaces sodium chloride.)

The process of the present invention permits the pickling of large, whole pieces of v g tables, fruits and meats in very short times (about 0.001 to about 72 hours), which r sults in savings.

Importantly, in the process of the present invention, green stock comprising continuous compact inner tissues (e.g. whole vegetables) need not be sliced, diced, halved, quartered, etc. to achieve full brine absorption. Nonetheless, when the green stock is in the form of whole pieces and the green stock contains a member which inhibits the infusion of dissolved solids and calcium into and the transfer of gases out of the green stock, such as in a cucumber where the cucumber skin may inhibit such transfer, it is preferred that the green stock is pricked to improve transfer. For example, the common size pickling whole cucumbers may be pricked between about 8 and about 20 times.

The process of the present invention, once the brine has been prepared, can be carried out at any temperature at or below the temperature at which the brine boils. Nonetheless, it is preferred that the process is either carried out at a temperature less than about 10 F above the freezing point of the brine or between about 100 F and the boiling point of the brine. It is more preferred that when the brine is used in the higher temperature range that the temperature is between about 125 F and the boiling point of the brine.

The processes of the present invention do not "lose" product as some prior art process do, and these processes provide firm textured, "crunchy", freshly-made type products.

Once immersed in a brine according to the present invention, the calcium, acids and other materials in the brine are rapidly infused into the green stock. These components are rapidly and evenly absorbed into the green stock and prevent the green stock from fermenting. Moreover, this same brine prevents any of the water-acid soluble green stock tissues which enter the brine from

The rapid absorption and binding of calcium ions to the green stock's pectinaceous tissues maintains its original intact continuous texture. Moreover, the brine itself, in the process of the present invention, is non-fermenting and thus does not produce and saturate the "pickle" with carbon dioxide.

After brining, according to the process of the present invention, the "pickled" product has the desired salt level for a finished product. Thus, there is no need to "desalt", repack or a combination thereof to reach the desired finished product salt level. The calcium bound to the green stock's pectin remains and assures that the product retains its firm texture throughout storage without any additional steps.

The process of the present invention prevents fermentation, bloating and softening simultaneously, while producing a crisp product in a substantially aseptic process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention is applicable to a variety of foods -- fruit, vegetable and meat based green stock -- as well as a variety of pickle types produced, i.e. Sour, Sweet-sour, Dill, Polish dill, Kosher dill, etc.

The following ingredient list shows the variety and functionality of ingredients useful in the present invention:

Acidulants: As a solid or as a water miscible liquid. Useful acidulents include Lactic, Acetic, Citric, Tartaric, Fumaric, Malic, Adipic, Ascorbic and Succinic acids, Sodium acetate and diacetate, and Glucono delta lactone.

To produce the brines used in the practice of the present invention it is useful to add a quantity of acid (an acid

approved for use in food processes) with or before adding the calcium to the water to make the brine. It is preferred that the weight of the calcium salt used is between about 5 and about 45 % of the acid. It is more preferred that the weight of the calcium salt used is between about 10 and about 30 % of the acid. One technique that has been useful in the practice of this invention is the addition of the calcium salt used with about three times as much acid, by weight, in the initial addition and then adding sufficient acid to the brine to make the calcium about 10 % of the acid. It is believed that this acid helps solubilize/suspend the calcium in the brine.

Calcium (salts and water/acid calcium soluble compounds): As a solid or as a water miscible liquid. Useful calcium materials include calcium chloride, oxide, sulfate, lactate, acetate and gluconate.

Salts (as humectants and flavoring agents): As a solid or as a water miscible liquid. Useful salts include: sodium chloride, potassium chloride, magnesium chloride, calcium chloride.

Spices (for flavoring and/or coloring) in a dry and/or a liquid extract form: ground, extracted and dried; with or without carriers and adjuncts; essential spice oils/flavors extracted and/or dried with or without carriers and adjuncts; from any parts and variety of the plants used. Without limitation, the following spices currently used in pickling are useful in the process of the present invention: basil, bay, celery, cloves, coriander, dill, garlic, marjoram, mustard, onion, black/white/red pepper, turmeric, and combinations thereof.

Flavors: every applicable, water/acid soluble single or compounded flavor as a solid or as a water miscible liquid, either

from natural and/or artificial sources, with or without carrier or adjunct(s) i.e.: Vinegar, Polish dill, individual/combination spice flavors, etc. It is preferred that the flavors used are both heat and acid stable.

Sweeteners (as flavorings and humectants): every applicable, water/acid soluble sweetening compound in dry or in a water miscible liquid form, either of natural or synthetic origin, including poly/di/mono-saccharides such as maltodextrins, sugar, fructose, glucose, xilitol and sodium, potassium and calcium saccharin, aspartame, etc.

Flavor enhancers: every applicable natural and/or artificial ingredient/compound of dry or water miscible liquid form, with or without carriers or adjuncts added: i.e. mono-sodium glutamate (MSG); dry yeast; yeast extract; autolyzed yeast; miso; hydrolyzed plant and animal proteins; sodium inosinate and guanilate.

Powder flow/anti-caking agents: every applicable, currently used ingredient/compounds: i.e. silica; silica-gels and silicates; tri-calcium phosphate; microcrystalline cellulose; vegetable oils and stearates; calcium sulfate; and hydrolyzed cereal solids.

Buffering agents: every applicable, water/acid soluble compound in a dry or in a water miscible liquid form including, e.g. mono-calcium phosphate and tri-sodium citrate.

Chemical preservatives (in addition to the hydroxy- and saturated alkyl carboxylacids set forth above as "acidulants") every applicable, FDA approved/regulated water/acid soluble solid compound, which functions best in a pH range between 2.5 and 4.5 as an anti-microbial, anti-fungal or anti-mycotic agent: i.e.

sodium benzoate, calcium/sodium salts of propionic and sorbic acids, sodium bisulfite.

It has been also noted that when foodstuffs are heated to a temperature of greater than about 150 F in a high acid environment their structural integrity is frequently lost. Thus, for example, many foodstuffs become very mushy when they are heated extensively in the presence of 1 to 2 %, by weight, acid. This loss of structural integrity is more extensive when the foodstuffs are heated to a temperature of greater than about 170 F in a high acid environment or when the acid concentration of the environment is increased to about 4 to 5 %.

However, by infusing the foodstuff which is to be subjected to a high acid environment (such as an environment wherein the total acidity is greater than 2 % of the mass of the environment, especially foodstuffs that are to be subjected to extensive heating in a high acid environment) with Ca^{2+} salts equal to or more than about 10 %, by weight, of the acid in the acid environment, the foodstuff is able to maintain its structural integrity and maintain a crisp mouthfeel texture even when heated in such a high acid environment. It is therefore desirable to infuse foodstuffs that are to be extensively heated in an about 2 % acid environment with at least about 2000 ppm Ca^{2+} salts and it is desirable to infuse foodstuffs that are to be extensively heated in an about 4.4 % acid environment with at least about 4400 ppm Ca^{2+} salts.

One application of this process for making a foodstuff capable of maintaining its structural integrity even when the foodstuff is to be extensively heated in a high acid environment is in the preparation of pickle relishes wherein the flavorings

used frequently require a high acid level and manufacturers may wish to pasteurize the relish product to assure themselves that the product is reasonably free from contamination.

In the application of the present process to maintaining a foodstuff's structural integrity in the presence of heat and a high acid environment, it is preferred that the foodstuff is infused with at least about one tenth part of calcium ions for each part of an acid moiety in the high acid environment.

EXAMPLE I

The following ingredients were combined in the ratios set forth below:

<u>Ingredient</u>	<u>as is, %</u>
a 50:50 mixture of potassium and sodium chloride, fine granulated	51.10
Calcium sulfate (dihydrate), USP	30.00
Malic acid, anhydrous	8.00
Sodium benzoate	4.35
Tumeric	2.75
Dill flavor	1.30
Ground cloves	1.25
Ground coriander	1.25
TOTAL	100.00

EXAMPLE II

Washed, quartered cucumbers (spears) were pickled by putting 650 parts of cucumber spears in a clean one quart mason jar. The mason jar containing the cucumber spears was placed in a thermo-stated ultra-sonic bath set at about 150 F.

Separately, 298 parts of water were heated to boiling and 29 parts of the Example I formulation was added to the boiling water with agitation. Once the Example I formulation was substantially dispersed/dissolved in the boiling water, 22.5 parts of a 20%

aqueous media, at which point the brine comprised about 2000 ppm Ca^{2+} . Next, the entire solution was transferred to the mason jar containing the cucumber spears.

After the aqueous media was added to the mason jar, the jar was sealed with a cap that was attached to a vacuum pump, the vacuum pump was turned on to reduce the pressure in the mason jar to about 4-5 inches of mercury, and the ultra-sonic transducer was turned on. The cucumber spears were kept under these conditions for about 15 minutes, at which point the vacuum pump was turned off and the jar containing the spears was removed from the ultra-sonic bath.

The spears processed according to this process were much firmer than spears not processed, and, by a calcium ion specific measuring technique, were found to contain about 1800 ppm Ca^{2+} . Additionally, the spears processed in a manner similar to the above were observed to yield a total microorganism plate count of less than 10 colonies per gram of pickled green stock and the total yeast and mold plate count was also less than 10.

In similar experiments, it has been observed that the above process takes about twice as long to complete without the ultra-sonic treatment, and with the ultra-sonic treatment but without the reduced pressure, the above-described process takes a substantially longer time to complete. Furthermore, it is believed that the treatment with ultra sonic sound waves improves the suspension of the ingredients and reduces microbial growth.

This process has also been used to prepare pickles from: cucumbers (pricked whole, chunks, and slices); cabbage (shredded); pearl onions (stems and bottoms removed); zucchini (quartered lengthwise); mushrooms (small whole pieces); tomato

slices; mixed vegetables (sliced carrots, small stemless peppers, cauliflower pieces and olives); brussel sprouts (whole); and five inch asparagus stalks.

EXAMPLE III

Washed, quartered cucumbers (spears) were pickled by putting 650 parts of cucumber spears in a clean approximately one quart vacuum bag.

Separately, 298 parts of water were heated to boiling and 29 parts of the Example I formulation was added to the boiling water with agitation. Once the Example I formulation was substantially dispersed/dissolved in the boiling water, 22.5 parts of a 20% vinegar solution was added to the aqueous media, mixed with the aqueous media and then the entire solution was transferred to the bag containing the cucumber spears, which was sealed.

The sealed bag was placed in a freezer at between about -10 and about 0 F for about 4 to 6 hours. At that point, the bag containing the spears was removed from the freezer and defrosted to room temperature. When the room temperature treated spears were removed from the bag, they were firm, and exhibited freeze-thaw stability (pickled cucumber spears were defrosted and refrozen four times in their original container without a significant loss of flavor or texture).

Nonetheless, to date, this embodiment of the present invention has not been successfully applied to whole (i.e. not pricked, quartered, or sliced) cucumbers.

It is believed that the mechanism of the freezing method of rapidly infusing green stock with dissolved solids and calcium relies upon the development of very small ice crystals.

EXAMPLE IV

Pickles prepared from cucumber slices that contained about 500 ppm calcium ions started to become soft after about two to three weeks when stored at about 100 F. In contrast, the pickles of the present invention that were made from cucumber slices and contained about 1500 ppm calcium ions, as measured, showed some signs of softening after six weeks, but were still firm and "crisp".

Pickles containing about 500 ppm calcium ions and pickles containing about 1500 ppm calcium ions were stored at about 70 F. Neither of the pickle samples stored at 70 F appeared to lose their crisp texture during 12 weeks.

EXAMPLE V

The following ingredients were combined in the ratios set forth below:

<u>Ingredient</u>	<u>%</u>
Salt, fine ground	61.90
Calcium sulfate, anhydrous	13.96
Malic acid, anhydrous	8.78
Lactic acid, (60% acid level on silicon dioxide)	5.20
Natural dill flavor	3.98
Tartaric acid, anhydrous	2.70
Sodium benzoate	1.96
Garlic flavor	0.58
Ground cloves	0.58
Ground turmeric	0.36
TOTAL	100

EXAMPLE VI

Washed cucumbers were sliced and 325 parts of the fresh sliced cucumbers were placed in an about one pint mylar pouch.

separately, 150 parts of water were heated to boiling and 25 parts of the Example V formulation was added to the boiling water with agitation. Once the Example V formulation was substantially dispersed/dissolved in the boiling water, the aqueous media, which then comprised about 2250 ppm calcium ions, as measured, was transferred to the mylar pouch containing the cucumber slices. The mylar pouch containing the cucumber slices and the brine was then heat sealed and there was substantially no head-space in the sealed pouch. The sealed pouch was allowed to sit at room temperature for about 45 minutes to cool. Thereafter, the pouch containing the cucumber slices and brine was frozen solid by being placed in an about 5 to 15 F freezer for about six hours. Once the pouch's contents were frozen, the pouch was removed from the freezer and allow to thaw at room temperature, which thawing took about four hours. Once the pouch had reached about room temperature, a sample of the slices was removed and the slices treated according to this process were found to be fully translucent, fully cured having a typical pickle flavor profile and a crisp, full texture. Additionally, the slices were found to contain about 2400 ppm calcium ions.

EXAMPLE VII

The following ingredients were combined in the ratios set forth below:

<u>Ingredient</u>	<u>%</u>
Salt, fine ground	54.97
Malic acid, anhydrous	15.01
Tartaric acid, anhydrous	11.36
Calcium sulfate, dihydrate	9.74
Lactic acid, (50% acid level on silicon dioxide)	3.54
Natural flavor	2.82
Sodium benzoate	1.39
Xanthan gum	0.72
Ground bay	0.44
Ground cloves	0.21
TOTAL	100

EXAMPLE VIII

Washed cucumbers were diced (1/8 x 1/8 x 1/4 inches), and 720 parts of the diced cucumbers were placed in a clean one quart Mason jar.

Separately, 75 parts, by weight, of the Example VII formulation were combined with 205 parts of boiling water. This combination was mixed until the Example VII formulation was substantially dispersed/dissolved in the boiling water. The resulting aqueous media contained about 6400 ppm of calcium.

The aqueous media containing about 6400 ppm of calcium was added to the 720 parts of diced cucumbers in the clean Mason jar and the combination was then mechanically mixed. After mixing, the temperature of the diced cucumber-aqueous media combination was found to be about 110 F.

The Mason jar containing the diced cucumber-aqueous media combination was then transferred to a hot water bath set at about 175 F. When the centre of the Mason jar was found to have reached a temperature of about 175 F, the Mason jar and contents were removed from the hot water bath and hermetically sealed. Thereafter, the sealed Mason jar was placed in an approximately

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90 F water bath. A relish made by a process similar to this was found to contain about 2000 ppm calcium and about 2 percent total acidity, and the product was found to have a crisp texture.

What we claim is a:

1. A pickle composition comprising:
 - a) green stock; and
 - b) at least about 700 ppm added calcium.
2. A pickle composition according to claim 1 wherein the green stock is a cucumber.
3. A pickle composition according to claim 1 which further comprises at least about 0.6 %, on a weight basis, of an acid.
4. A pickle composition according to claim 1 wherein the pickle composition comprises a microbial contamination total plate count of less than about 10 colonies per gram of pickle.
5. A pickle composition according to claim 3 wherein said acid is selected from the group consisting of lactic acid, salts of lactic acid, acetic acid, salts of acetic acid, citric acid, salts of citric acid, tartaric acid, salts of tartaric acid, fumaric acid, salts of fumaric acid, malic acid, salts of malic acid, adipic acid, salts of adipic acid, ascorbic acid, salts of ascorbic acid, succinic acid, salts of succinic acid, and combinations thereof.
6. A pickle composition according to claim 1 which further comprises between about 0.6 and about 0.9 %, on a weight basis, of an acid.

7. A pickle composition according to claim 6 wherein said acid is selected from the group consisting of lactic acid, salts of lactic acid, acetic acid, salts of acetic acid, citric acid, salts of citric acid, tartaric acid, salts of tartaric acid, fumaric acid, salts of fumaric acid, malic acid, salts of malic acid, adipic acid, salts of adipic acid, ascorbic acid, salts of ascorbic acid, succinic acid, salts of succinic acid, and combinations thereof.

8. A pickle composition comprising:

- a) green stock;
- b) at least about 1000 ppm added calcium.

9. A pickle composition according to claim 8 wherein the green stock is a cucumber.

10. A non-fermentative pickling process comprising the steps of:

- a) preparing a brine wherein said brine comprises at least about 1500 ppm calcium;
- b) placing green stock in said brine; and
- c) treating said green stock in said brine in a manner effective to infuse said green stock with at least about 1000 ppm Ca^{2+} within about 72 hours.

11. A non-fermentative pickling process according to claim 10 wherein said treatment to infuse said green stock with at least about 1000 ppm Ca^{2+} is effective to infuse said green stock within about 12 hours

12. A non-fermentative pickling process according to claim 10 wherein said treatment effective to infuse said green stock with said calcium concentration comprising the step of placing said green stock in said brine in a reduced pressure environment.
13. A non-fermentative pickling process according to claim 12 wherein said process further comprises the step of maintaining the temperature of said green stock in said brine in said reduced pressure environment above about 125 degrees Fahrenheit.
14. A non-fermentative pickling process according to claim 11 wherein said process further comprises the step of treating said green stock in said brine in said reduced pressure environment with ultra sonic sound waves.
15. A non-fermentative pickling process according to claim 12 wherein said pressure in said reduced pressure environment is less than about 10 inches of mercury.
16. A non-fermentative pickling process according to claim 12 wherein said pressure in said reduced pressure environment is less than about 5 inches of mercury.
17. A non-fermentative pickling process according to claim 10 wherein said treatment is effective to infuse said green stock with said calcium concentration comprising the step of freezing said green stock in said brine.
18. A process according to Claim 10 wherein said brine further

19. Pickled green stock pickled by the process of Claim 10.
20. A non-fermentative pickling process comprising the steps of:
 - A) formulating a pickling composition comprising calcium and an acidulant wherein there are about one tenth part of calcium for each part acidulant in said pickling composition;
 - B) heating a measured volume of water to about boiling;
 - C) producing a brine solution by adding a measured quantity of said pickling composition to said measured volume of water at about boiling so that said measured quantity of said pickling composition, when combined with said measured volume of water, is effective to produce a brine comprising at least 1500 ppm calcium, and at least 0.3% acidulant;
 - D) placing a quantity green stock effective to fill between about 40 and about 75 % of a container's volume into a container;
 - E) adding said brine to said container in a manner effective to fill between about 90 and about 100 % of said container's volume with green stock and brine;
 - F) sealing said container after said green stock and said brine have been added to said container; and
 - G) treating said green stock and said brine in a manner effective to infuse said green stock with at least about 1000 ppm Ca^{2+} within about 72 hours of sealing said container.
21. A foodstuff able to maintain its structural integrity when heated to a temperature of greater than about 150 F in the presence of an acid concentration of at least about 2 % which comprises:

- A) green stock; and
- B) at least about 2000 ppm of a Ca^{2+} salt.

22. A foodstuff able to maintain its structural integrity when heated to a temperature of greater than about 150 F in the presence of an acid concentration of at least about 4 % which comprises:

- A) green stock; and
- B) at least about 4400 ppm of a Ca^{2+} salt.

23. A foodstuff able to maintain its structural integrity when heated to a temperature of greater than about 170 F in the presence of an acid concentration of at least about 2 % which comprises:

- A) green stock; and
- B) at least about 2000 ppm of a Ca^{2+} salt.

24. A foodstuff able to maintain its structural integrity when heated to a temperature of greater than about 170 F in the presence of an acid concentration of at least about 4 % which comprises:

- A) green stock; and
- B) at least about 4400 ppm of a Ca^{2+} salt.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 89/05267

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
IPC(5): A23B 47/027, 49/08, 7/05, 7/10
U.S.Cl.: 426/238, 321, 327, 615

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
U.S.	426/238, 321, 327, 615

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 3,578,466 (Luckmann et al) 11 May 1971 see entire document.	1-5,8,9 7,21-24
X	US, A, 4,789,558 (Winkler et al) 6 December 1988 see entire document.	1,2,8,9 10,12,19
Y	US, A, 2,801,925 (Fisher) 06 August 1957 see column 3, lines 5-16.	10-13,15 16,18,20
Y	US, A, 3,743,523 (Bodine) 03 July 1973 see column 1, lines 5-10.	14
A	US, A, 4,614,655 (Hashino et al) 30 September 1986 see entire document.	
A	US, A, 3,136,642 (Backinger et al) 09 June 1964 see entire document.	

- Special categories of cited documents: ¹⁰
- “A” document defining the general state of the art which is not considered to be of particular relevance
- “E” earlier document but published on or after the international filing date
- “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- “O” document referring to an oral disclosure, use, exhibition or other means
- “P” document published prior to the international filing date but later than the priority date claimed

- “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- “&” document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

02 February 1990

Date of Mailing of this International Search Report

16 MAR 1990

International Searching Authority

ISA/US

Signature of Authorized Officer

DREW WORKMAN, EXAMINER

